TiO_2 composited with carbon nanofibers or nitrogen-doped carbon nanotubes synthesized using coal fly ash as a catalyst: Bisphenol-A photodegradation efficiency evaluation.

Supplementary information

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(S1)

Table S1 Volume of titanium isopropoxide and mass of NCNTs or CNFs used for the synthesis of the various composites

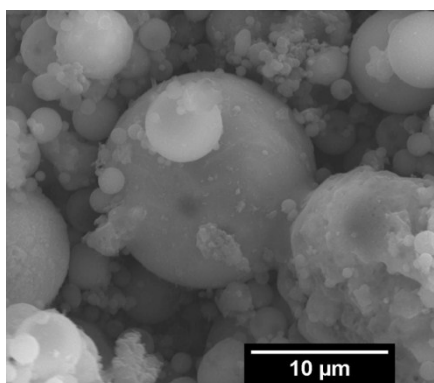| Sample	Volume of $Ti[OCH(CH_3)_2]_4$ (ml)	Mass of CNFs (g)	Mass of NCNTs (g)
TiO_2	1	0	0
TiO_2/1%CNFs	1	0.0026	0
TiO_2/5%CNFs	1	0.014	0
TiO_2/20%CNFs	1	0.065	0
TiO_2/1%NCNTs	1	0	0.0026
TiO_2/5%NCNTs	1	0	0.014
TiO_2/20%NCNTs	1	0	0.065

(S2)

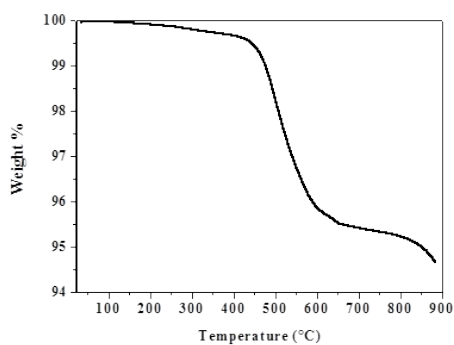Fig. S1 SEM image of CFA.

(S3)

Fig. S2 TGA thermogram of CFA.

(S4)

Table S2 Photoluminescence emission intensities and band gap energies (Tauc's plot) of the various potential photocatalysts

Material	PL emission intensity (a.u)	Band gap (eV)
TiO_2	101	3.25
TiO_2/1%_CNFs	85	3.19
TiO_2/5%_CNFs	72	3.19
TiO_2/20%_CNFs	55	3.19
TiO_2/1%_NCNTs	80	3.24
TiO_2/5%_NCNTs	36	3.19
TiO_2/20%_NCNTs	24	3.12

(S5)

The characteristic band energy of TiO_2 nanoparticles was observed at 3.25 eV, while the band energies of the TiO_2_CNFs/NCNTs composites were found to be slightly lower. For instance, the TiO_2_CNFs composites showed the least improvement i.e. all had band energies of 3.19 eV. On the other hand, the TiO_2_NCNTs composites had lower band energies as the % NCNT in the composite was increased (i.e. they decreased from 3.24 to 3.12 eV as the % NCNT was increased from 1% to 20%).
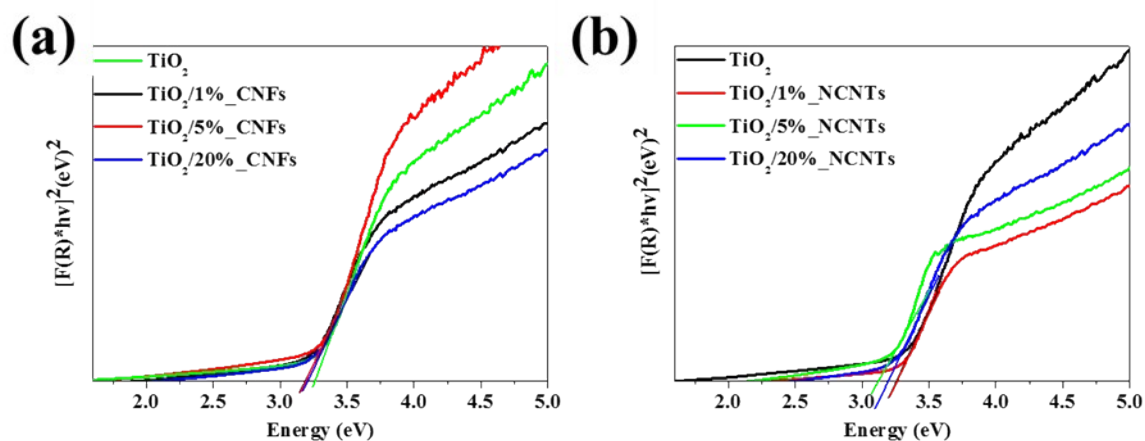

Fig. S3 UV-DRS Tauc's plots of TiO_2 and various potential photocatalysts.

(S6)

The kinetics of the photocatalytic decomposition of organic contaminants assumes the form of a simple pseudo first-order reaction, where the rate limiting step is the rate at which the active radical species are produced.[1] Indeed, this is true but in photocatalysis, the depth at which light can penetrate is another important factor to be considered.[1] Therefore in order to avoid using excess quantity of catalyst, it is necessary to optimize the mass of catalyst used for the efficient photodegradation of BPA. The effect of the mass of catalyst (using unbound TiO_2) for the photodegradation of BPA (100 ppm BPA, 50 ml solution, pH 7 for 2 h at 22 °C) was investigated in the range of 20-100 mg per 50 ml BPA solution.

Here it was observed that the % BPA that was photodegraded increased with increasing mass of the catalyst (i.e. unbound TiO_2) in the range from 20-60 mg per 50 ml solution, with the optimum catalyst mass being 60 mg (**S6**). However, the photodegradation efficiencies of the unbound TiO_2 catalyst at 80 and 100 mg per 50 ml BPA solution were lower than those that were obtained at 40 and 60 mg per 50 ml. Indeed, several studies have found that increasing the mass of photocatalyst per volume of solution did not necessarily always result in increased efficiency. For example, Muruganandham *et al*. have reported an increase in the photocatalytic decolorization of reactive yellow 14 azo dye as a function of increased catalyst mass/volume at a range of 1-4 g/l, whereas at between 4 and 6 g/l, they observed that the activity had plateaued off.[2] Similarly, it has been reported that the photodegradation efficiency of BPA increased as a function of increased mass of catalyst per volume of solution i.e. up to 500 mg, after which it plateaued off and then decreased from 600 to 1000 mg.[2]
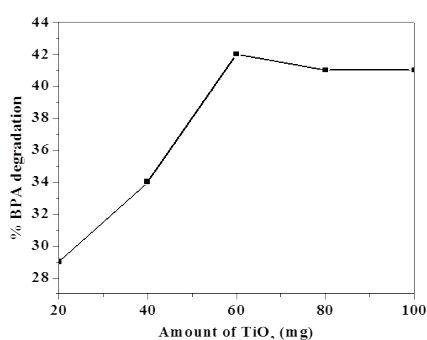

Fig. S4 The effect of the mass of photocatalyst (i.e. unbound TiO_2) on the photodegradation of 50 ml of 100 ppm solution (pH 7) of BPA in water at 22 °C for 2 h.

(S7)

Here reactions were conducted in the pH range of 3 to 13, where the highest photoactivity that was measured was for the solution at pH 13. This was attributed to that fact that at high pH there are more hydroxyl ions which upon interaction with photogenerated positively charged holes yield hydroxyl radicals.[2] In photocatalysis hydroxyl radicals are the foremost oxidizing agents when created in abundance, hence the rate at which BPA was photodegraded at pH 13 increased. This conclusion has been reached by several authors.[1,3–5]

Consequently, pH 13 was selected as the optimum pH for the photodegradation of BPA, which also happened to be the pH at which BPA was the most soluble in water. It is noteworthy that the optimal pH obtained in this study would not be applicable in real life applications.
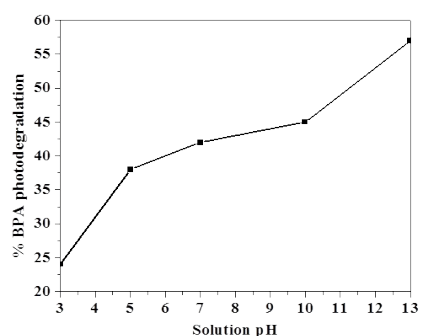

Fig. S5 The effect of solution pH on the % BPA of 50 ml of 100 ppm that was photodegraded in water using 50 mg TiO_2 as a photocatalyst, at 22 °C for 2 h.

(S8)

The concentration of pollutants in water systems varies. This, therefore, necessitates a determination of the photocatalyst efficiency at different substrate (e.g. BPA) concentrations. Thus the effect of the initial BPA concentration on the ability of unbound TiO_2 to photodegrade it, in the range of 40 ppm to 140 ppm, was investigated. Here an inverse relationship between the % BPA that was photodegraded and the BPA concentration was observed.

Here the least % BPA that was photodegraded was observed when the initial concentration of BPA was 140 ppm, while the highest was for when 40 ppm BPA was used. It is thought that when such large concentrations of BPA were used, they were adsorbed onto the catalyst surface and impeded light from reaching it and initiating photocatalytic reactions. Furthermore, it is suggested that with the catalyst so covered the BPA itself absorbed the incoming radiation. Indeed, several authors have observed similar trends to these.[2,3,6,7]
Nevertheless, in view of the practical need to clean wastewater with high concentrations of BPA, 100 ppm was selected as the substrate concentration to be used for evaluating the photodegradation efficiencies of the various TiO_2_CNFs/NCNTs composites.
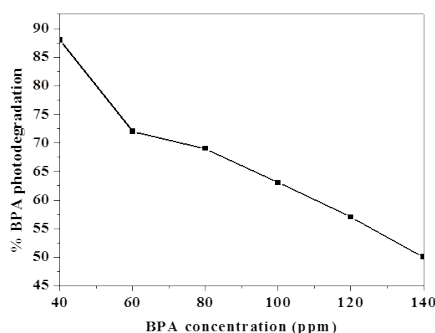

Fig. S6 The effect of the initial concentration of BPA on the % BPA photodegraded in a 50 ml solution at pH 7 using 60 mg TiO_2 at 22 °C for 2.

(S9)

Temperature is one of the environmental factors that could influence the photodegradation efficiency. Hence the effect of temperature was studied within the ranges of 22 and 50 °C using TiO_2 as was the case with all other optimization experiments. There was not much difference in the efficiencies of the experiments conducted at different temperatures to make any kind of conclusion.

Therefore for the purposes of evaluating the photoactivity of the various potential TiO_2_CNFs/NCNTs catalysts, 22 °C (room temperature) was chosen. Thus the optimal conditions that were used for evaluating the photocatalytic efficiencies of the various potential TiO_2_CNFs/NCNTs catalysts are summarized in Table 2.
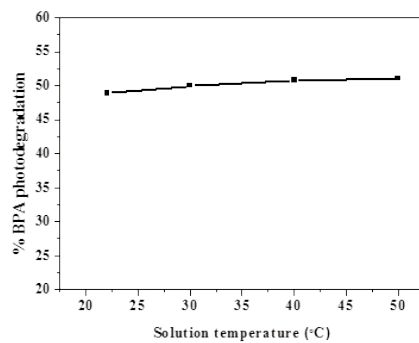
Fig. S7 Effect of temperature on the photodegradation of 50 ml of 100 ppm neutral solution of BPA in water at 22 °C using 50 mg TiO_2 for 2h.

(**S10**)

Table S3 Summary of the photodegradation efficiencies of the various TiO_2_CNFs/NCNTs photocatalysts after 4 h (X_{4h}, %).

Sample	X_{4h} (%)
TiO_2	59
TiO_2/1%_CNFs	64
TiO_2/5%_CNFs	90
TiO_2/20%_CNFs	36
TiO_2/1%_NCNTs	75
TiO_2/5%_NCNTs	98
TiO_2/20%_NCNTs	42

References

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